



## Full Length Article

# Catalytic effect of ion-exchanged calcium on steam gasification of low-rank coal with a circulating fluidized bed reactor



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## ABSTRACT

Calcium ion exchange was performed in Indonesian low-rank coal using saturated aqueous solutions of  $\text{Ca}(\text{OH})_2$  at  $30.0 \pm 0.1$  °C without pH adjustment. The  $\text{Ca}^{2+}$  concentration and pH were monitored during ion exchange. A coal product was obtained with 3.2 mass%  $\text{Ca}^{2+}$ . Gasification of the ion-exchanged samples was conducted in a circulating dual bubbling fluidized bed (CDBFB) reactor at 700 °C, 800 °C, and 900 °C. Coal carbon conversion into carbonaceous gases ( $\text{CO}$ ,  $\text{CO}_2$ ,  $\text{CH}_4$ , and  $\text{C}_2$  hydrocarbons) using the  $\text{Ca}^{2+}$ -exchanged coal achieved 78% at 900 °C in the CDBFB. The Ca catalyst led to the greatest rate enhancement at 800 °C, resulting in a twofold increase in the gas product yield compared to that without Ca.

A comparison of carbon conversion between the CDBFB and fixed-bed reactors revealed that the conversion value using the CDBFB at 700 °C was very small. Regarding an examination of this influence in detail, it seems that the existing  $\text{H}_2$  adhered primarily to the active sites of the char, and the use of  $\text{Ca}^{2+}$ -exchanged coal led to a reverse shift reaction.

## 1. Introduction

Improving the efficiency of coal is a high priority for reducing  $\text{CO}_2$  output. Systems that have performed well include ultra-supercritical pulverized coal combustion, integrated coal gasification combined cycle (IGCC), integrated gasification fuel cells (IGFC), and poly-generation. Moreover, the utilization of low-rank coal, a potentially plentiful resource, is also important to establish a stable future energy supply. Despite this, at present, there is little economic incentive to burn low-rank coal because of the associated production costs. Consequently, in the publication *Strategic Technical Platform for Clean Coal Technology (STEP CCT)*, the New Energy and Industrial Technology Development Organization (NEDO) in Japan describes the development of the IGCC system using low-rank coal gasification at or below 900 °C in the presence of catalysts. In addition, advanced IGCC and advanced IGFC systems with exergy recuperation was proposed in order to increase the thermal efficiency of IGCC systems [1–7]. In regards to these systems, steam recovers the exhaust heat from a solid oxide fuel cell or

a gas turbine. Hot exhaust gas cools greatly in an entrained-flow bed reactor [8]. Therefore, our group adopted a circulating dual bubbling fluidized bed (CDBFB) reactor as it induces a heat insulation effect is obtained. This causes the exhaust gas in the system to maintain its temperature when the CDBFB reactor is used.

As for the strong volatile–char interaction and reduction of tar emissions, a downer pyrolyzer has a major influence on subsequent steam gasification using a novel triple-bed combined circulating fluidized bed (TBCFB) reactor [1,9,10]. For instance, steam gasification of Adaro coal (particle size,  $d_p = 0.5\text{--}1.0$  mm) char at 700–900 °C was studied using a lab-scale TBCFB [9,10].

Coal pyrolysis has been performed previously in a drop-tube reactor (DTR) [11–16] and a downer reactor [17–19]. The reactivity of Loy Yang coal chars and those blended with coal at 50%–85% ratios was investigated using a DTR at 900 and 950 °C [15]. The reactivities of Na and Ca in the raw coal were investigated using the same DTR at 850–900 °C [20]. However, catalytic steam gasification of  $\text{Ca}^{2+}$ -exchanged low-rank coal using the CDBFB and the TBCFB reactor has not

*Abbreviations:* CDBFB, circulating dual bubbling fluidized bed; FB, fixed bed; IGCC, integrated coal gasification combined cycle; IGFC, integrated gasification fuel cells; STEP CCT, *Strategic Technical Platform for Clean Coal Technology*; NEDO, the New Energy and Industrial Technology Development Organization; TBCFB, triple-bed combined circulating fluidized bed; DTR, drop-tube reactor; XRD, X-ray diffraction

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been studied.

As regards a catalyst with steam gasification of coal, achieving low-temperature gasification requires application of a catalyst. Our previous results show that catalytic steam gasification of low-rank coal with ion-exchanged Ca prepared from saturated  $\text{Ca}(\text{OH})_2$  solution was an excellent catalyst for use in a fixed-bed reactor [21]. Therefore, we expected this material to show similar performance in a CDBFB reactor. The present study thus examines the effect of Ca catalyst on steam gasification of a sub-bituminous coal in a CDBFB system. If the inexpensive catalyst can decrease the gasification temperature and increase the gasification rate, it may present several advantages, such as the circulation of large amounts of coal particles and enhanced-exergy recuperation in the CDBFB system.

## 2. Experimental

### 2.1. Coal samples

Indonesian sub-bituminous coal (Adaro) was used, denoted AD, because this coal was one of standard samples in the STEP CCT project. The coal sample was air-dried at room temperature, crushed, and sieved to obtain particles with a size range of 150–250  $\mu\text{m}$ . Table 1 shows the results from compositional analyses. Table 2 summarizes the metal analysis (Na, Al, Si, K, Ca, and Fe) of the coal and shows that the main constituent elements were Si, Al, Fe, and Ca.

### 2.2. Catalyst materials and ion-exchange methodology

Saturated  $\text{Ca}(\text{OH})_2$  (Wako Pure Chemical Industries, Ltd.) was used as the precursor for the ion-exchanged Ca catalyst. The size fraction of coal samples as received was in the range of 150–250  $\mu\text{m}$ . The samples were used without any pretreatment.

As in our previous study [21], a saturated  $\text{Ca}(\text{OH})_2$  solution was added to a suspension of coal particles and deionized water, which was held at constant temperature ( $30.0 \pm 0.1$  °C) without pH adjustment. The  $\text{Ca}^{2+}$  concentration and pH of the mixture during stirring were monitored using  $\text{Ca}^{2+}$ -selective and pH electrodes (Table 3). The  $\text{Ca}^{2+}$ -exchange reaction used 60 g of coal per reaction for a total of 5 exchange reactions. The initial cation concentration was 649 mg Ca/L ( $\text{Ca}^{2+}$  ions). The amount of  $\text{Ca}^{2+}$  ions actually exchanged was calculated using the following equation:

Exchange amount (mass %)

$$\frac{\text{change in concentration before and after the reaction (mg)}}{\text{weight of coal after drying (mg)}} \times \frac{\text{the solution quantity (L)}}{\text{weight of coal after drying (mg)}} \times 100 \quad (1)$$

After completion of the ion-exchange reaction, the  $\text{Ca}^{2+}$ -exchanged coal was separated by filtration, washed with high-purity water, dried under vacuum at 60 °C, and then classified according to particle size (150–250  $\mu\text{m}$ ). The recovery ratio of  $\text{Ca}^{2+}$ -exchanged coal to total coal amount ( $60 \text{ g} \times 5 \text{ times} = 300 \text{ g}$ ) was 72%–75%. The total amount of obtained  $\text{Ca}^{2+}$ -exchanged coal was about 220 g.

**Table 1**  
Ultimate and proximate analyses of Adaro.

Ultimate analysis (mass%, daf <sup>a</sup> )					Proximate analysis (mass%, dry)			
C	H	N	S	O <sup>b</sup>	Ash	VM <sup>c</sup>	FC <sup>b,c</sup>	
67.8	5.1	0.44	0.14	26.5	2.5	46.7	50.8	

<sup>a</sup> daf = dry ash free.

<sup>b</sup> Determined by difference.

<sup>c</sup> VM = volatile matter; FC = fixed carbon.

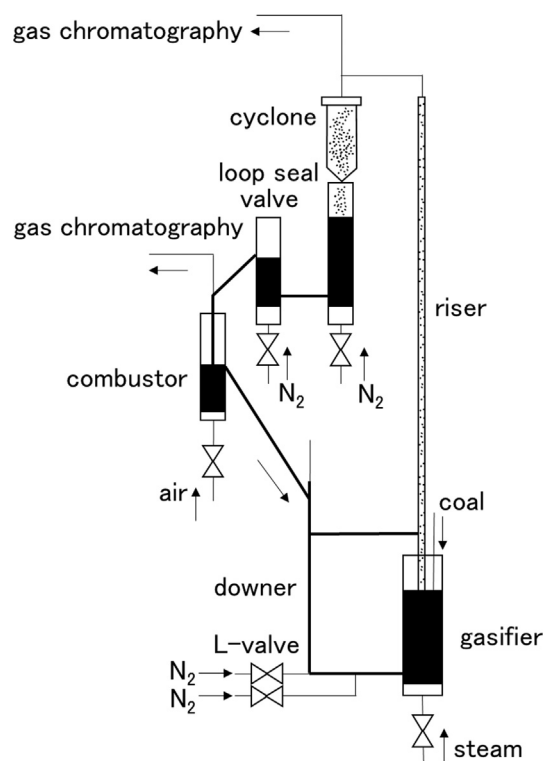
**Table 2**  
Metal concentrations in the Adaro coal sample.

Metal concentration <sup>a</sup> (mass%, dry)					
Na	Al	Si	K	Ca	Fe
0.010	0.18	0.41	0.014	0.18	0.24

<sup>a</sup> Determined by inductively coupled plasma emission spectroscopy (ICP-ES) after acid leaching of ash obtained by pyrolysis at 815 °C.

**Table 3**  
 $\text{Ca}^{2+}$  ion-exchange reaction conditions.

Coal (g)	Saturated calcium hydroxide solution			Reaction temperature (°C)
	$\text{Ca}(\text{OH})_2$ (g)	Deionized water (ml)	$\text{Ca}^{2+}$ (mg/L)	
60.00	3.6	3000	649	$30.0 \pm 0.1$



**Fig. 1.** Schematic drawing of the circulating dual bubbling fluidized bed reactor used in this study.

### 2.3. Circulating dual bubbling fluidized bed reactor and product gas analysis

A CDBFB reactor was used for our experiments [22]. Fig. 1 shows a schematic drawing of the CDBFB reactor. The size and reaction temperature of the apparatus are shown in Table 4, and the gasification conditions are shown in Table 5. The coal feed rate was 1.0 g/min. The samples were supplied ( $\text{H}_2\text{O}/\text{coal} = 1.4\text{--}1.6 \text{ kg/kg}$ , 20 vol%  $\text{H}_2\text{O}/\text{N}_2$ ) and silica sand heating-medium particles (150–250  $\mu\text{m}$ ; 95 mass%  $\text{SiO}_2$ ) into the top of the fluidized bed in the gasifier with a screw feeder in the CDBFB. Our previous steam gasification results using woody biomass using a CDBFB reactor showed that the increase of carbon conversion with S/C was not observed at higher S/C ( $1 < \text{S}/\text{C} < 3$ , i.e., 12–36 vol% steam concentration) [22]. Accordingly, 20 vol% steam concentration (S/C = 1.5) was adopted. The formed gas and tar captured by the siliceous and unconverted char were transported

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